Reply to "Comment on 'Evidence for the immobile bipolaron formation in the paramagnetic state of the magnetoresistive manganites'"

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Zhao *et al.* (Phys. Rev. B **62**, R11 949 (2000)) reported studies of the oxygen-isotope effects on the intrinsic resistivity and thermoelectric power in the paramagnetic state of several ferromagnetic manganites. The isotope effects on the intrinsic electrical transport properties are not consistent with a simple small-polaron hopping mechanism, but can be well explained by a model where there coexist immobile bipolarons and thermally-excited small polarons. Recently, Banerjee *et al.* (Phys. Rev. B **68**, 186401 (2003)) wrote a Comment on our paper, where they misunderstood our theoretical model, erroneously thinking that we explain the electrical transport in the paramagnetic state as due to bipolaron hopping. They confuse large polarons with small bipolarons, use incorrect conditions for bipolaron formation, and even incorrectly reproduce our data. We show that the model used in the Comment is inconsistent with any features of the observed oxygen-isotope effects. More evidence is provided to support the theoretical model used in our original paper.

Experimental evidence for small polaron charge carriers in the paramagnetic state was provided by transport measurements [1]. It was found that the activation energy E_ρ deduced from the conductivity data is one order of magnitude larger than the activation energy E_s obtained from the thermoelectric power data. Such a large difference in the activation energies is the hallmark of the small-polaron hopping conduction [1]. In our recent paper [2], we reported studies of the oxygen-isotope effects on the intrinsic resistivity and thermoelectric power in the paramagnetic state of several ferromagnetic manganites. The isotope effects on the intrinsic electrical transport properties can be well explained by a model where there coexist immobile bipolarons and thermally-excited small polarons. In our theoretical model, the electrical transport in the paramagnetic state is due to small polaron hoping, but such polarons are thermally excited from localized bipolaronic states. Recently, Banerjee *et al.* [3] wrote a Comment on our paper, where they misunderstood our theoretical model, erroneously thinking that we explain the electrical transport in the paramagnetic state as due to bipolaron hopping. They confuse large polarons with small bipolarons, use incorrect conditions for bipolaron formation, and even incorrectly reproduce our data. We show that the model used in the Comment is inconsistent with any features of the observed oxygen-isotope effects. More evidence is provided to support the theoretical model used in our original paper [2].

Fig. 1 shows the temperature dependence of the resistivity of the oxygen-isotope exchanged films of $La_{0.75}Ca_{0.25}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$. The data are the same as those reported in our original paper [2]. The only difference is that the resistivity is plotted as a function of T/T_C in our original paper [2], where T_C is the Curie temperature. Comparing the data shown here and the data shown in Fig. 1 of the Comment [3], we can clearly see that they do not reproduce our data correctly. Further, the authors of the Comment [3] fit their incorrectly reproduced data by

$$\rho = DT \exp(E_\rho/k_B T), \qquad (1)$$

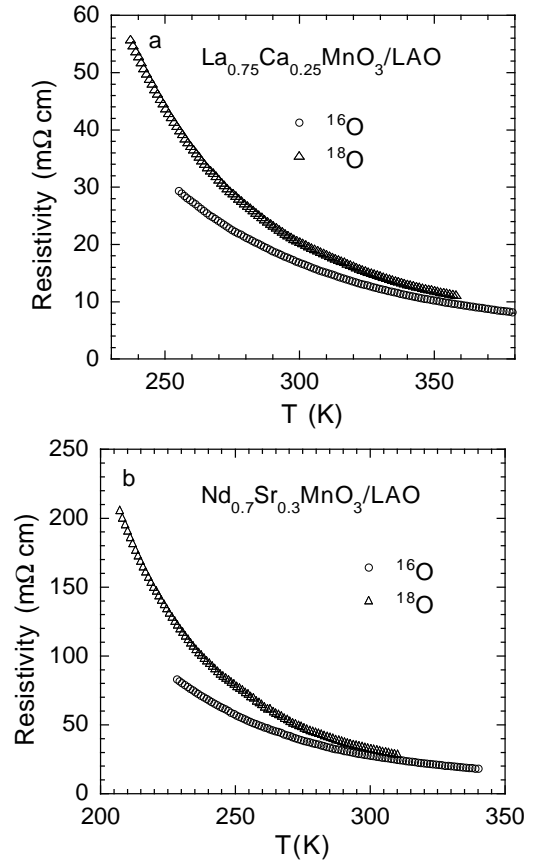where the coefficient D is inversely proportional to the characteristic phonon frequency ν_0.

FIG. 1. The temperature dependence of the resistivity of the oxygen-isotope exchanged films of a) $La_{0.75}Ca_{0.25}MnO_3$ and b) $Nd_{0.7}Sr_{0.3}MnO_3$. The data are the same as those reported in Ref. [2].

We can also fit the data of Fig. 1 by Eq. 1. The curves fitted to the resistivity data of the oxygen-isotope exchanged $La_{0.75}Ca_{0.25}MnO_3$ films are shown in Fig. 2. The best fits yield the fitting parameter $D = 7.36\times10^{-7}$ $\Omega cm/K$ for the ^{16}O sample and $D = 6.15\times10^{-7}$ $\Omega cm/K$ for the ^{18}O sample. We can see that the D value for the ^{16}O sample is larger than that for the ^{18}O sample by 20%. Since $D \propto 1/\nu_0 \propto \sqrt{M}$, we expect that the D value for the ^{16}O sample should be smaller than that for the ^{18}O sample. This is in sharp contrast with the isotope effect on the D value obtained above. This implies that Eq. 1 is not a relevant formula to describe the electrical transport in the paramagnetic state of $La_{0.75}Ca_{0.25}MnO_3$. If the authors of the Comment would provide the fitting parameters for both isotope samples, they would not claim that their model could better explain our data.
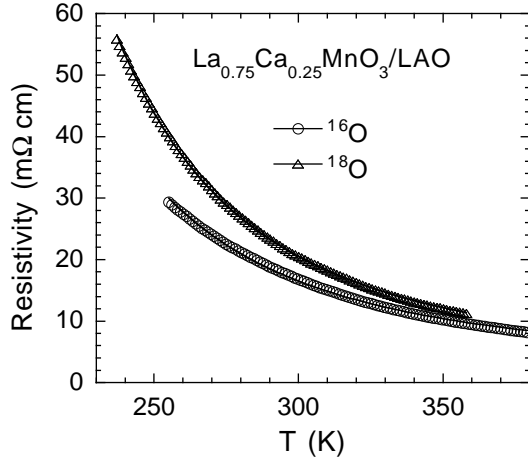

FIG. 2. The temperature dependence of the resistivity of the oxygen-isotope exchanged films of $La_{0.75}Ca_{0.25}MnO_3$. The solid lines are the curves best fitted by Eq. 1. The fitting parameter D for the ^{16}O sample is larger than that for the ^{18}O sample by 20%.

In fact, we have shown [2] that if k_BT is less than the polaron bandwidth W_p and only thermally excited polarons from localized bipolaron states contribute to the electrical transport in the paramagnetic state, the resistivity is given by

$$\rho = \frac{C}{\sqrt{T}} \exp(E_\rho/k_BT), \qquad (2)$$

where $E_\rho = E_a + E_s$, $C = (ah/e^2\sqrt{k_B})(1.05W_p)^{1.5}/h\nu_o$, a is the hopping distance, E_s is the activation energy for polarons to be thermally excited from localized bipolaron states, and E_a depends on the polaron binding energy E_p and bare hoping integral t. The quantity C should strongly depend on the isotope mass M and decrease with increasing M. This is because W_p decreases strongly with increasing M according to $W_p = 12t \exp(-\Gamma E_p/\hbar\omega_o) = 12t \exp(-g^2)$, where Γ is a constant (<1) [4,5]. In our

original paper [2], we fit the resistivity data of the ^{16}O and ^{18}O samples of $La_{0.75}Ca_{0.25}MnO_3$ by Eq. 2 and find that the parameter C for the ^{16}O sample is larger than that for the ^{18}O sample by 34%, in agreement with the theoretical model (Eq. 2). In fact, this model can quantitatively explain [2] the combined isotope effects on C and on E_s.

On the other hand, if small polarons are bound to localized impurity states rather than to localized bipolaron states, E_s would be independent of the isotope mass in the zero-order approximation according to Austin and Mott [6]. In our original paper, we have only considered this possibility [2]. Here, we shall consider the other possibility, that is, a polaron is bound to an impurity site with the screened Coulombic interaction reduced by a factor of the static dielectric constant ϵ_s (continuous medium approximation). The binding energy of the impurity state is given by [7]

$$E_c = \frac{13.6}{\epsilon_s^2} \frac{m^*}{m_e} eV, \qquad (3)$$

where m^* is the effective mass of a polaron and m_e is the mass of a free electron. The thermally excited polaron density from the impurity states is [7]

$$n = (2N_d)^{1/2}(m^*k_BT/2\pi\hbar^2)^{3/4}\exp(-E_c/2k_BT), \quad (4)$$

where N_d is the dopant concentration. The thermoelectric power is correspondingly given by [6]

$$S = \frac{k_B}{e}(E_s/k_BT + \alpha'), \qquad (5)$$

where $E_s = E_c/2$ and α' is a constant depending on the kinetic energy of the polarons and on the polaron density [6]. With the mobility of polarons [8] $\mu \propto \nu_o/k_BT \exp(-E_a/k_BT)$, we finally have

$$\rho = BT^{0.25} \exp(E_\rho/k_BT), \qquad (6)$$

where $E_\rho = E_a + E_c/2$ and $B \propto W_p^{3/4}/\nu_o$.

In Fig. 3 we fit the resistivity data of the isotope exchanged $La_{0.75}Ca_{0.25}MnO_3$ by Eq. 6. The best fits yield $B = 1.13\times10^{-4}$ $\Omega cm/K^{0.25}$ for the ^{16}O sample and $B = 0.89\times10^{-4}$ $\Omega cm/K^{0.25}$ for the ^{18}O sample. It is clear that the B value for the ^{16}O sample is larger than that for the ^{18}O sample by 27%. This is in agreement with the theoretical prediction. If we assume that ν_o is inversely proportional to the square root of the reduced mass of the manganese and oxygen atoms, ν_o will decrease by 4.6% upon replacing ^{16}O by ^{18}O. Using the oxygen-isotope effect on B and the relation $B \propto W_p^{3/4}/\nu_o$, we find that W_p for the ^{18}O sample is smaller than that for the ^{16}O sample by 46%. The exponent of the oxygen-isotope effect on W_p is $\beta_O = -d\ln W_p/d\ln M_O = 3.2$, where M_O is the oxygen mass.
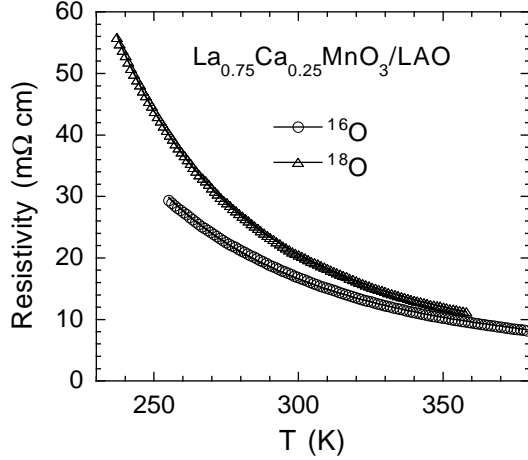
FIG. 3. The temperature dependence of the resistivity of the oxygen-isotope exchanged films of $La_{0.75}Ca_{0.25}MnO_3$. The solid lines are the curves best fitted by Eq. 6. The fitting parameter B for the ^{16}O sample is larger than that for the ^{18}O sample by 27%.

From the thermoelectric power data of the isotope exchanged $La_{0.75}Ca_{0.25}MnO_3$, we have found that [2] $E_s = 13.2$ meV for the ^{16}O sample and $E_s = 18.7$ meV for the ^{18}O sample. Then we have $E_c = 26.4$ meV for the ^{16}O sample and $E_c = 37.4$ meV for the ^{18}O sample. Using Eq. 3 and $W_p \propto 1/m^*$, we find $\beta_O = 3.0$, close to the value (3.2) deduced from the resistivity data above. This appears to indicate that this model can quantitatively explain the isotope effects.

From $W_p = 12t \exp(-\Gamma E_p/\hbar\omega_o) = 12t \exp(-g^2)$, we can easily show that $\beta_O = g^2/2.6$. Here we have used the fact that ω_o is inversely proportional to the square root of the reduced mass of the manganese and oxygen atoms. Using $\beta_O = 3.0$-3.2, one has $g^2 = 7.8$-8.3. Assuming that the bare effective mass of charged carriers is about $0.5m_e$, we find that the effective mass of polarons m^* is about $1500m_e$, which seems unlikely.

It is worthy of noting that Eq. 3 is valid only if the Bohr radius $r_B = 0.53\epsilon_s m_e/m^*$ Å is significantly larger than the interatom distance (2 Å) [7]. Using $\epsilon_s = 20$ (Ref. [11]) and $m^* = 1500m_e$, we get $r_B = 0.007$ Å and $E_c = 51$ eV. The calculated $E_c = 51$ eV is over three orders of magnitude larger than the measured one. The calculated $r_B = 0.007$ Å implies that the continuous medium approximation does not hold. Thus Eq. 3 cannot be applied to doped manganites unless the effective mass of charged carriers is close to m_e. This is possible only if the charged carriers are not small polarons, in contradiction with the large isotope exponent β_O and the observed small polaron hopping conduction. Therefore, the model where polarons are bound to impurity sites with the screened Coulombic interaction (continuous medium approximation) cannot explain the observed isotope effects on the intrinsic electrical transport properties.

On the other hand, if polarons are bound into much heavier bipolarons [9], the random potentials produced by dopants can completely localize bipolaron band. The minimum separation between the polaron and bipolaron bands is $\Delta = 2(1 - \Gamma)E_p - V_c - W_p$, where V_c is the Coulombic repulsion between bound polarons [5]. It is clear that the value of Δ could be less than 0.1 eV, in agreement with the measured value of about 30 meV in $La_{0.75}Ca_{0.25}MnO_3$.

Within the same model where polarons are bound into the localized bipolaron states [2], we have also determined the bandwidths for the isotope exchanged samples of $La_{0.75}Ca_{0.25}MnO_3$, that is, $W_p = 49.0$ meV for ^{16}O sample and $W_p = 38.8$ meV for the ^{18}O sample. The values of W_p lead to $\beta_O = 2.0$ and $g^2 = 4.6$. Then the bare hopping integral t is calculated to be 0.41 eV from the values of g^2 and W_p. The inferred value of t is in reasonable agreement with the band structure calculation [12]. Further, since $E_s = \Delta/2$ and $\Delta = 2(1 - \Gamma)E_p - V_c - W_p$, the change of E_s due to the oxygen isotope substitution is $\delta E_s = \delta\Delta/2 = -\delta W_p/2$. With $\delta W_p/2 = -11.2$ meV for $La_{0.75}Ca_{0.25}MnO_3$, one has $\delta E_s = 5.5$ meV, in quantitative agreement with the value (5.5±0.6 meV) deduced independently from the thermoelectric power data [2].

The electron-phonon coupling constant g^2 can be also determined from optical conductivity data. It is shown [5] that the optical conductivity contributed from polaronic charged carriers exhibits a broad peak feature at an energy of $E_m = 2g^2\hbar\omega_o$. Jung et al. [10] have identified the polaronic conductivity and determined the value of E_m as a function of doping x in $La_{1-x}Ca_xMnO_3$ system. From their results [10], one can easily see that $E_m \simeq 0.7$ eV for $x = 0.25$. If we take $\hbar\omega_o = 0.074$ eV (Ref. [2]), we have $g^2 = 4.7$, in quantitative agreement with the value (4.6) deduced from the isotope effects.

In our data analyses [2], we assume that bipolarons are completely localized by random potential due to dopants and defects, and the conductivity is only contributed from thermally excited small polarons. The authors of the Comment misunderstand our theoretical model, erroneously thinking that we explain the conductivity in the paramagnetic state as due to bipolaron hopping. Furthermore, they confuse large polarons with small bipolarons. From the value of α' in Eq. 5, which is found to be less than 1 for our samples, the authors of the Comment conclude that [3] our data are consistent with small polaron hopping conduction mechanism, but disagree with bipolaron hopping conduction mechanism. This is incorrect. The value of α' can only discriminate between small polaron and large polaron conduction mechanisms. Bipolarons are not equivalent to large polarons.

Finally, the arguments [3] against the formation of bipolarons in doped manganites do not have scientific ground. The authors of the Comment argue that bipolarons cannot be formed in doped manganites because there is not enough disorder. We do not believe that

3

disorder is a required condition for the formation of bipolarons. Bipolarons can be formed when electron-phonon interactions are strong enough to overcome direct Coulombic interaction between two polarons [5]. The authors of the Comment [3] also mistakenly think that the charge disproportionality is a necessary condition for the formation of bipolarons. Intersite bipolarons do not involve any charge disproportionality. In this Comment, there is also a mistake in the criterion for the adiabatic or nonadiabatic hoping conduction mechanisms. The bare bandwidth should be used to compare the parameter $\phi = (k_B T E_p/\pi)^{1/4}(\hbar\omega_o/\pi)^{1/2}$. But the authors of the Comment [3] use the effective polaron bandwidth instead of the bare bandwidth to compare the parameter ϕ. It is clear that the bare bandwidth is larger than ϕ so that the adiabatic hopping conduction is relevant in doped manganites.

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